Anomalous grain boundary physics in polycrystalline $CuInSe_2$: the existence of a hole barrier

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Abstract

First-principles modeling of grain boundaries (GB) in $CuInSe_2$ semiconductors reveals that an energetic barrier exists for holes arriving from the grain interior (GI) to the GB. Consequently, the absence of GB holes prevents electrons from recombining at the GB defects. At the same time, the GI is purer in poly materials than in single crystal, since impurities segregated to the GB's. This explains the puzzle of the superiority of polycrystalline $CuInSe_2$ solar cells over their crystalline counterpart. We identify a simple and universal mechanism for the barrier, arising from reduced *p-d* repulsion due to Cu-vacancy surface reconstruction. This discovery opens up for future design of superior polycrystalline devices.

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Keywords:

Photovoltaic solar cells [1] and other optoelectronic devices often necessitate the use of (rather expensive) *single-crystalline* active materials, because the analogues, low-cost *polycrystalline* substances [2], tend to exhibit poor carrier transport. A polycrystalline material [2] is made of small crystallites joined at their surfaces via grain boundaries (GB's). These interfaces tend to become sinks for both chemical impurities and structural defects that segregate there from the grain interior (GI) during growth. In polycrystalline Si and GaAs these GB defects form effective recombination [2] centers for the optically generated electrons and holes, thus diminishing and even eliminating carrier transport. Attempts to utilize polycrystalline semiconductors such as Si or GaAs in solar cells [1] thus rest on various schemes for partial chemical passivation of the GB's. However, the device efficiency is always lower than that of the corresponding single-crystalline devices. A notable exception is polycrystalline $CuInSe_2$ solar cells [3, 4], where todays cell efficiencies ($\sim$20% [4]) outperform the best single-crystal devices ($\sim$13% [5]), even though no deliberate passivation of the GB's is attempted. This puzzle in polycrystalline $CuInSe_2$ [3, 4] and related polycrystalline materials [6] attracted recently considerable attention [6, 9–11], because the understanding of the natural GB passivity in ternary chalcopyrites could lead in the future to the deliberate design of optoelectronic devices based on low-cost polycrystalline materials.

Much of the thinking about GB's is based on their similarity to surface structures [2]. Various electronic measurements [12, 13] have long demonstrated that the free surface [12] and heterojunction [13] of chalcopyrite $Cu(In,Ga)Se_2$ exhibit a "type inversion", whereby the surface region becomes electron-rich, even though the interior is hole-rich. Attempts to identify a novel crystallographic phase responsible for such a type-inversion have failed [9]. Similarly, the existence of some kind of "filter" impeding the motion of one type of carrier into the GB/surface has been noted in Hall effects and in conductivity measurements on polycrystalline $CuGaSe_2$ [11]. Spatially-resolved photoluminescence measurements [14] show that the emission characteristic of GB's in polycrystalline $CuInSe_2$ is pinned even when the excitation power is increased, suggesting that one or both types of the photogenerated carriers do not penetrate the GB. Similar barriers have been detected in polycrystalline CdTe [15]. The prevailing thought [9–11, 14] about the origin of such barriers is the classical picture [7, 8, 16] assuming the existence of some *charged defects* near the GB surface, which would set up an electrostatic barrier, impeding the motion of GI electrons (holes) into the GB regions if the GB is negatively (positively) charged by ionized acceptors (donors).

For $CuInSe_2$, Schuler *et al.* [11] suggest generic surface donors, whereas Romero *et al.* [14] postulate surface acceptors, and Niemegeers *et al.* [10] propose an "ordered defect phase" containing a high concentration of (unknown) acceptors. Herberholz *et al.* [9] offer a scenario where anion vacancy V_{Se}^{+} (donor) drives out Cu and forms a dipolar complex V_{Se}^{+}+V_{Cu}^{-}. These proposals for *charged* surface defects in $CuInSe_2$ [9–11, 14] and other polycrystalline systems [6–8] are highly system- and growth-specific, whereas the existence of GB/surface barriers is generic to a large class of semiconductors in various growth regimes. Furthermore, to explain the existence of a hole barrier [11] in chalcopyrites one has had to assume a *positively charged surface donor*, yet conventional chalcopyrite growth conditions [3, 4] are known to create cation-poor surface which forms [7] *negatively charged acceptors*.

We have identified an *intrinsic* and *charge neutral* mechanism for a spontaneous formation of hole barriers at the GB/surface of chalcopyrites, which could explain why such polycrystalline cells can not only *approach* the cell efficiency of their crystalline counterpart (as is the case for Si and GaAs [1]), but also *exceed* it. The explanation is based on the recognition that the most robust characteristic of a GB, beyond any specifics of its composition, size, and detailed defect chemistry, is its manifestation of *surface-like structure* [2]. Unlike covalent binary semiconductors, the stable surface of chalcopyrites is *polar* [17]. Polar surfaces exhibit [18] universal reconstruction patterns involving rows of *vacancies* [17]. We show here via first-principles calculations of model $CuInSe_2$ GB's that the Cu vacancy reconstruction always depresses the valence band at the GB, thus impeding holes from entering it. Whereas such barriers for hole transport from the GI to GB are normally thought to have the adverse effect of impeding grain-to-grain transport [17, 19] by depriving the GB from holes, this also diminishes electron-hole recombination at the chemical traps that segregate into the GB, potentially leading to unimpeded *electron* transport through the GB. We conclude that the local reconstruction at the GB expels holes, thus creating a "free zone" for fast electron transport. Future design of recombination-free zones via engineering of a barrier to one carrier type can open the way to the utilization of polycrystals in high-performance devices.

Perfect semiconductor polar surfaces, such as (001) or (111) [18] made of alternate anion/cation layers would exhibit a nominal charge imbalance [20] which would lead to an "electrostatic catastrophe" [20], i.e., to a divergence of surface energy. This is avoided through the formation of reconstruction patterns whose universal feature [21] is the appearance of charge-balancing *vacancy rows* [18]. In zinc-blende semiconductors, the *nonpolar*

(110) surface is more stable than polar (001) and (111) surfaces [17] because the formation of vacancy rows necessitated by polar surfaces is energetically costly [17, 18]. Because of the different d-bonding in $CuB^{III}X_2^{VI}$ chalcopyrites [19], Cu vacancies have low formation energy both in the bulk and at the polar (112) surface [17]. Consequently, both theory [17] and experiments [22] show that the *polar* surface (112) is the most stable surface in chalcopyrites, consisting of charge-neutralizing surface V_{Cu}^0 rows.

Since no structural models are available for the GB's in chalcopyrites, we model them via their most generic feature described above – their polar surface characteristics. We therefore consider the following $CuInSe_2$ GB models: (a) A GB made of a single Cu-deficient (112) surface followed by vacuum [Fig. 1(a)]. (b) Two polar (112) surfaces facing each other with a spatial gap of 6.4 Å between them [Fig. 1(b)]. (c) A stacking fault structure where the two $CuInSe_2$ GI regions [see Fig. 1(c)] differ by an in-plane non-primitive translation $\tau_r = 0.5b$. The formation of this dislocation requires an interface defect. We have chosen the $(2V_{Cu}^{-}+In_{Cu}^{++})^0$ defect since this charge-neutral complex has the lowest formation energy in bulk $CuInSe_2$ [19], and the fact that high-quality polycrystalline $CuInSe_2$ [3, 4] is always Cu-deficient. All structures are optimized via first-principles total-energy minimization within the local density approximation (LDA) [23]. We investigate the type of wavefunction localization that ensues by calculating the planar-averaged wavefunction amplitude along the (112)-direction: $\rho_{j\mathbf{k}}(z) = \int dxdy\ \psi^*_{j\mathbf{k}}(\mathbf{r})\psi_{j\mathbf{k}}(\mathbf{r})$. The important quantity is how much of the wavefunction amplitude is localized at the GI and at the GB. This wavefunction amplitude is presented in Fig. 2 for the Γ-point states at the valence-band maximum (VBM) denoted E_v, at 1 eV below the VBM denoted E_v-1 eV, and at the conduction-band minimum (CBM) denoted E_c. Clearly, the wavefunctions of bulk $CuInSe_2$ [Fig. 2(d)] are extended throughout the crystal. Also the wavefunctions with energies E_v-1 eV and E_c in the surface structures [Fig. 2(a–c)] are extended throughout the material. In contrast, the hole wavefunction amplitude with energy E_v is absent from the GB/surface region. For a surface structure with an extended vacuum region, all wavefunctions have to decay to zero amplitude in the vacuum. Therefore, all three states in Fig. 2(a) are rather similar. The difference, however, is that the hole wavefunction at E_v avoids the very outermost Cu-poor surface layer in contrast with the wavefunction at E_v-1 eV. *The central feature of stable polar facets in chalcopyrite GB's is the disappearance of the amplitude of the valence-band-edge hole wavefunction from the GB and its displacements into the GI.* Hence, there is an effective barrier for the holes

to move from the GI to the GB.

The reason for the repulsion of holes from the GB interface region is the presence of Cu vacancies. The VBM of bulk $CuInSe_2$ consists of Cu d-orbitals (t_2 symmetry) which strongly interact with the Se p-orbitals (also t_2 symmetry), forming both the bonding and antibonding states in the valence band. The Cu,d–Se,p repulsion displaces therefore the antibonding VBM upwards [24]. Removal of Cu atoms from the GB/surface region diminishes this repulsion, and thus lowers the VBM. Since the CBM is mainly In,s–Se,p-like, the CBM is rather unaffected by the Cu,d–Se,p repulsion. Therefore, reconstruction of the GB interface via Cu vacancies lowers VBM at the GB's, thereby repelling the holes from this region. *The hole barrier arises due to the lack of d-electron states rather than from an electrostatic potential from a donor/acceptor environment.* The "type inversion" noted [12, 13] at the $CuInSe_2$ surface is enhanced by the same effect: Cu-vacancies lower the VBM at the surface, and thus repel holes. The fact that an energy barrier can be created with *electrically inactive* interface defects has a crucial physical importance for the charge transport in polycrystalline $CuInSe_2$, because *electrically active* donors/acceptors (as in the case for Si and GaAs surfaces) act normally as recombination channels near the GB and create highly resistive depletion regions [7].

The layer projected density-of-states [Fig. 3(a,b)] evinces that there is no valence-band d-states at the GB layer, whereas the valence band at the GI layers has considerable d-character. Since the Cu d-states dominate the density-of-state of the VBM in the material, the total VBM hole concentration is mainly located at the GI layers. Moreover, the p-like density-of-states at the VBM is energetically lowered at the GB compared to the corresponding states at the GI layer. This confirms that the Cu-deficient GB region affects the valence-band offset, and that the VBM holes are repelled from the GB. From the density-of-states of the GB and GI layers we estimate the hole energy barrier to be 0.2–0.4 eV [26].

It is important to notice that the existence of macroscopic amount of Cu vacancies is not only a central feature of $CuB^{III}X_2^{VI}$ chalcopyrite *surface*, but also a feature of all *non-stoichiometric bulk* chalcopyrites [19, 25]. Because of the low formation energy of the charge-neutral defect pair $2V_{Cu}^{-}+In_{Cu}^{++}$, [19] actual chalcopyrites are highly non-stoichiometric, exhibiting micro-phases made of units of $2V_{Cu}^{-}+In_{Cu}^{++}$ and $CuInSe_2$, resulting in $CuIn_5Se_8$, $CuIn_3Se_5$, and $Cu_2In_4Se_7$ phases. Calculations have shown [25] that due to the removal of Cu atoms from $CuInSe_2$ in forming these "ordered defect compounds" (ODC), the VBM

of the latter is lowered. Thus, accumulation of ODC at the GB/surface, noted experimentally [12], could also contribute to the hole barriers.

Hole barriers can also be contributed by *extrinsic* doping by neutral impurities. For example, it is known experimentally that growth of $CuInSe_2$ with Na-containing precursor [1, 27] places Na at the GB/surface and enhances the formations of polar (112) surfaces. Na is monovalent, just like Cu, but lacks *d*-orbitals. Thus, GB/surfaces with Na^0_{Cu} defects [27, 28] or $NaIn(S,Se)_2$ phases [28] will be electrically inactive and create a hole barrier due to the lack of *p*–*d* repulsion. Our calculations of a $2Na^0_{Cu}$ interface defect in the stacking-fault structure similar to that in Fig. 1(c) show [Fig. 3(c)] a reduced number of GB hole states at the VBM. The resulting GI/GB valence-band density-of-states is similar to the case of the Cu-deficient surface and the $(2V^-_{Cu}+In^{++}_{Cu})^0$ defect. Hence, a hole barrier created by charge-neutral Na^0_{Cu} defects at the surface can explain the puzzling improvement in solar-cell efficiency due to the presence of Na [1, 3, 4].

The LDA underestimates the self-interaction of localized *d*-states. To test the possible effect of this shortcoming on our results, we apply a self-interaction correction to the Cu-*d* electrons using the LDA+U approach [23]. Figure 3(d) compares the LDA and LDA+U density-of-states for the $2Na^0_{Cu}$ interface structure. Both computational methods yield qualitatively the same results with an effective hole barrier at the GB layer, and thus the Cu-*d* self-interaction error has no effects on our conclusions.

We conclude that the creation of a potential barrier at the GB for one type of carrier will impede electron-hole recombination at the GB despite the fact that this region could contain many defects. Photogenerated [26] GI/GB electron-hole pairs are dissociated at the GB, leading to diminished recombination there. In chalcopyrites, Cu vacancies are necessitated by the existence of an electrostatically stable *polar* surface or by stable ODC's. These vacancies create a barrier for holes through diminished *p*–*d* repulsion. This idea suggests that engineering of a GB "filter" made from electrically inactive defects that permits only one carrier type to penetrate the GB, holds the key to utilization of polycrystalline materials in transport devices.

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Figure captions

FIG. 1. Models of GB's in $CuInSe_2$: (a) A Cu-deficient (112) surface, (b) two Cu-deficient (112) surfaces, and (c) a stacking fault with $(2V_{Cu}^{-}+In_{Cu}^{++})^0$ interface defects. For comparison we show in (d) a perfect single-crystalline structure.

FIG. 2. Planar-averaged wavefunction amplitude $\rho_{j\Gamma}(z)$ at E_c, E_v, and E_v-1 eV in the (112)-direction for the structures in Fig. 1. Open and filled triangles indicate the positions of the Cu–In and the Se planes, respectively.

FIG. 3. Layer and angular projected density-of-states of a GI and a GB Cu–In–Se plane for (a,b) two structures of Fig. 1, and (c,d) a stacking fault with a $2Na_{Cu}^{0}$ interface defect. In (d) we have employed both the LDA (upper panel) and the LDA+U (lower panel) methods [23].

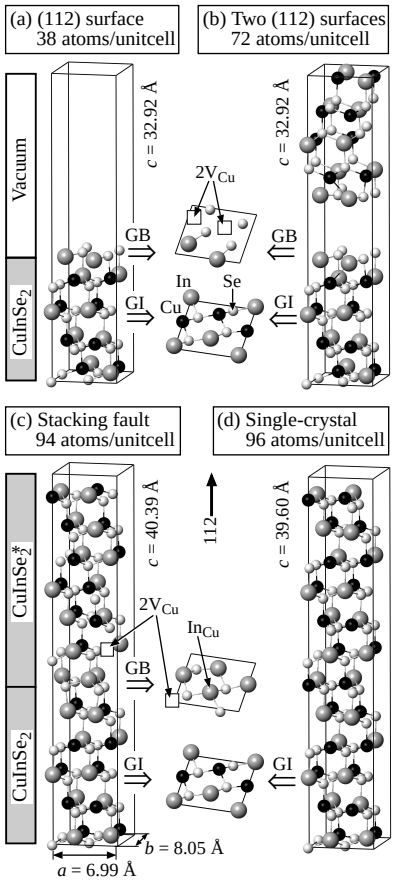
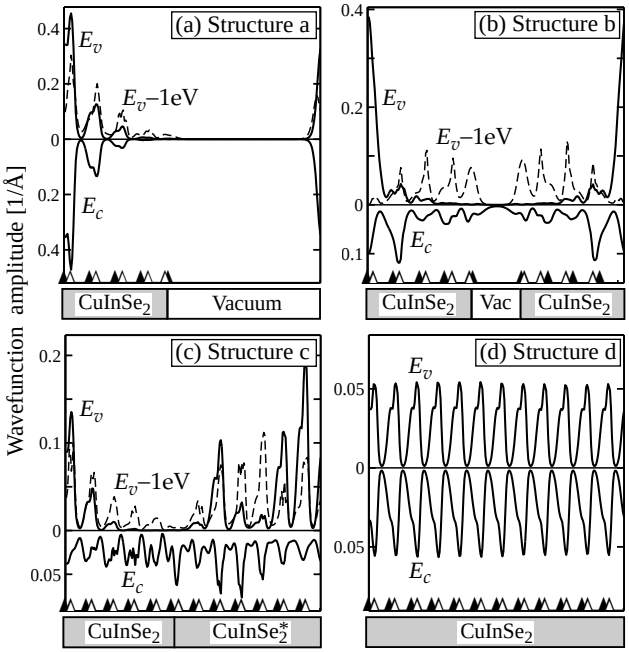


Fig. 1. C. Persson and A. Zunger, *"Anomalous grain boundary physics ... "* (2003).



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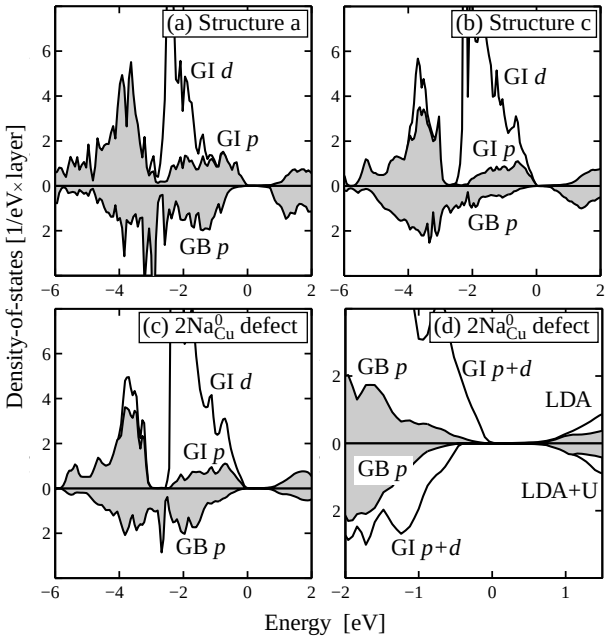

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